

FINAL TECHNICAL REPORT

**Measurements of Nitric Acid, Carboxylic Acids, and Selected Aerosol Species
for the NASA/GTE Pacific Exploratory Mission - West (PEM-WEST)**

NASA Research Grant NAG-1-1233

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1.0 Introduction

The research investigation funded through this grant to the University of New Hampshire was performed during a major field expedition conducted by the NASA Tropospheric Chemistry Program. The NASA Global Tropospheric Experiment (GTE) executed an airborne science mission (PEM-WEST A) aboard the NASA Ames DC-8 (717) over the Pacific Ocean during September/October 1991.

The atmosphere over the central Pacific Ocean is the only major region in the Northern Hemisphere that is relatively free from direct anthropogenic influence. Thus, this environment is ideally suited to study the natural biogeochemical cycles of carbon, nitrogen, ozone, sulfur, and aerosols without serious confounding problems related to anthropogenic emissions. Asian sources account for about 17% of the global budgets of nitrogen oxides (NO_x) and sulfur dioxide (SO_2). The Pacific Rim region therefore provides the opportunity to study the anthropogenic impact on natural atmospheric chemical cycles. PEM-WEST A flights were focused on contrasting the chemistry of "clean" air over the central Pacific with anthropogenically impacted air advected off the Asian continent.

The principal objectives of PEM-WEST A were to investigate the atmospheric chemistry of ozone (O_3) and its precursors, and to study important aspects of the atmospheric sulfur cycle over the western Pacific Ocean. Measurements conducted by the University of New Hampshire contributed directly to both of these objectives. Subsequent PEM-WEST field missions are planned by GTE in the mid-1990's to contrast atmospheric chemistry documented during PEM-WEST A with other time

periods.

This report presents preliminary findings from the PEM-WEST A field mission. Data interpretation is currently ongoing with the goal of manuscript submission of scientific results to a special issue of the Journal of Geophysical Research- Atmospheres in February 1994. The reader is strongly encouraged to review this suite of professional articles to appreciate the overall scientific findings and benefits of the PEM-WEST A field mission.

2.0 University of New Hampshire Measurements

In support of the PEM-WEST A airborne mission the University of New Hampshire flew instrumentation aboard the DC-8 research aircraft to provide measurements of the acidic trace gases nitric (HNO_3), formic (HCOOH), and acetic (CH_3COOH) acid. In addition, measurements were conducted to determine the major water-soluble ionic composition and the activities of ^{210}Pb and ^7Be in the atmospheric aerosol over the western Pacific Ocean.

The naturally occurring radioisotopes ^{210}Pb and ^7Be are useful source tracers in the following ways. ^{210}Pb is produced in the atmosphere from the decay of ^{222}Rn which emanates from the Earth's crustal materials. The ^{210}Pb thereby serves as a tracer of continental materials. In contrast, ^7Be has its source in the upper troposphere and stratosphere. There is about a factor of 10 gradient in ^7Be across this atmospheric region, with the highest activities found in the stratosphere. Thus, ^7Be is a good tracer of stratospheric inputs to the troposphere. The measurements of these two isotopes provided valuable information on source influences to the PEM-

WEST A study area.

3.0 PEM-WEST A Study Area and Flight Summary

A schematic representation of the PEM-WEST A study area is depicted in Figure 1. Overnight stops were made in Anchorage, Wake Island, and Hawaii during either the departing or returning transit flights. Science missions were conducted from three principal sites: Yokota Air Base, Japan; Hong Kong; and the island of Guam. Four science missions were conducted from Japan, two from Hong Kong, and three from Guam. The duration of each of the major science missions was approximately eight hours. A brief summary of these flights is given below.

		<u>Objective:</u>
Yokota Local #1	09/22/91	Aged marine air characterization.
Yokota Local #2	09/24/91	Characterization of continental outflow.
Yokota Local #3	09/26/91	Night/day photochemistry.
Yokota Local #4	09/27/91	Typhoon Mireille overflight.
Hong Kong #1	10/04/91	Characterization of continental outflow.
Hong Kong #2	10/06/91	Characterization of continental outflow.
Guam Local #1	10/11/91	Characterization of Southern Hemispheric aged air.
Guam Local #2	10/13/91	Characterization of equatorial low ozone region.
Guam Local #3	10/15/91	Night/day photochemistry.

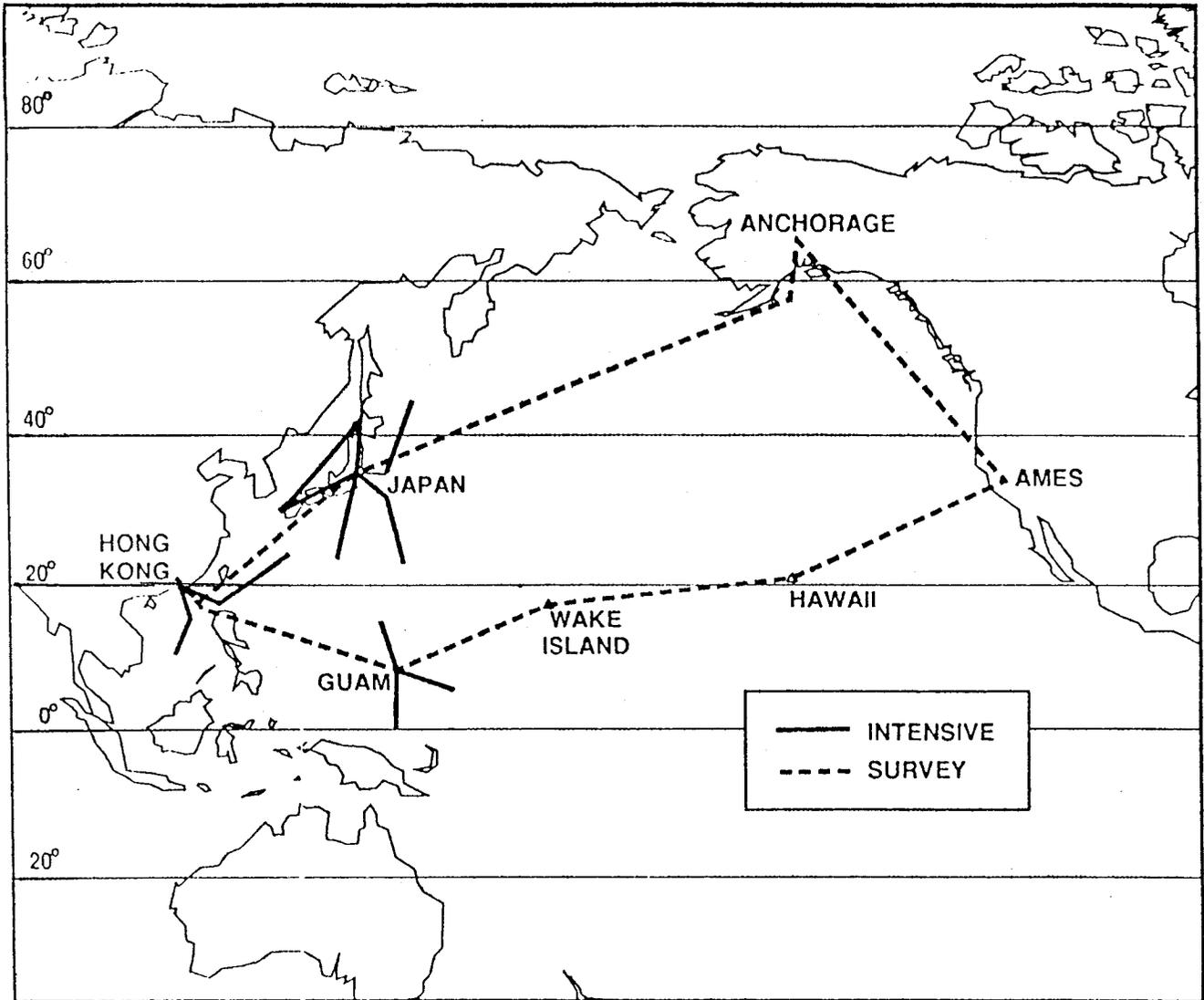


Figure 1. PEM-WEST A study regions over the Pacific Ocean.

4.0 Results from PEM-WEST A

"Clean" Western Pacific Air:

The PEM-WEST A science missions sampled a diverse suite of air masses over the western Pacific Ocean. Here we will divide the data into two major classifications to facilitate comparison of these air masses: (1) "clean" Pacific aged air and, (2) air influenced by Asian sources. More detailed comparisons, such as the chemical gradients over various air mass ages will be presented in manuscripts submitted to the Journal of Geophysical Research-Atmospheres special issue.

First, we present the chemical characteristics of trace acidic gases and selected aerosol species in "clean" Pacific aged air, and later they will be compared with results for continental influenced air mass compositions. To illustrate the aerosol composition of "clean" air we show (Table 1) typical molar mixing ratios (parts per trillion by volume, pptv) for nitrate (NO_3^-), non-sea-salt sulfate (nss SO_4^{2-}), ammonium (NH_4^+), and lead-210 (^{210}Pb , fCi scm^{-1}), along with that of carbon monoxide (CO, ppbv). Carbon Monoxide is generally a good indicator of combustion inputs to air masses.

The data compilation presented in Table 1 was selected primarily based on air mass isentropic trajectories which indicated that the sampled air masses had traveled over the Pacific Ocean for at least 10 days without contacting continental regions. The trajectories and CO data used in this report are available from the GTE PEM-WEST A data archive at NASA Langley Research Center. Carbon monoxide data used here was obtained by Mr. Glenn Sachse (Langley Research Center) and the trajectories were supplied by Dr. John Merrill (University of Rhode Island). A typical trajectory

Table 1. Aerosol Compositional Summary for Selected Species in "Clean" Air over the Western Pacific Ocean during Sept./Oct. 1991.

Location		^{210}Pb (fCi scm ⁻¹)	NO_3^- (pptv)	nss SO_4^{2-} (pptv)	NH_4^+ (pptv)	CO (ppbv)
Near-Continental Region:	BL	3.5-4.5	10-20	85-100	50-100	70
	FT	2.5-6.5	10-20	20-40	20-30	75
Guam Region:	BL	1.0-2.0	<5	20-30	30-40	75
	FT	1.0-4.0	10-20	10-30	<20	75
Southern Hemispheric: (Equatorial)	BL/	0.5-0.6	<5	10-30	30-40	70
	FT					

nss means non-sea-salt.

CO data courtesy of Glenn Sachse, NASA Langley Research Center, Hampton, VA.

BL means boundary layer.

FT means free troposphere.

Note: There was no discernible vertical gradient in Southern Hemispheric air.

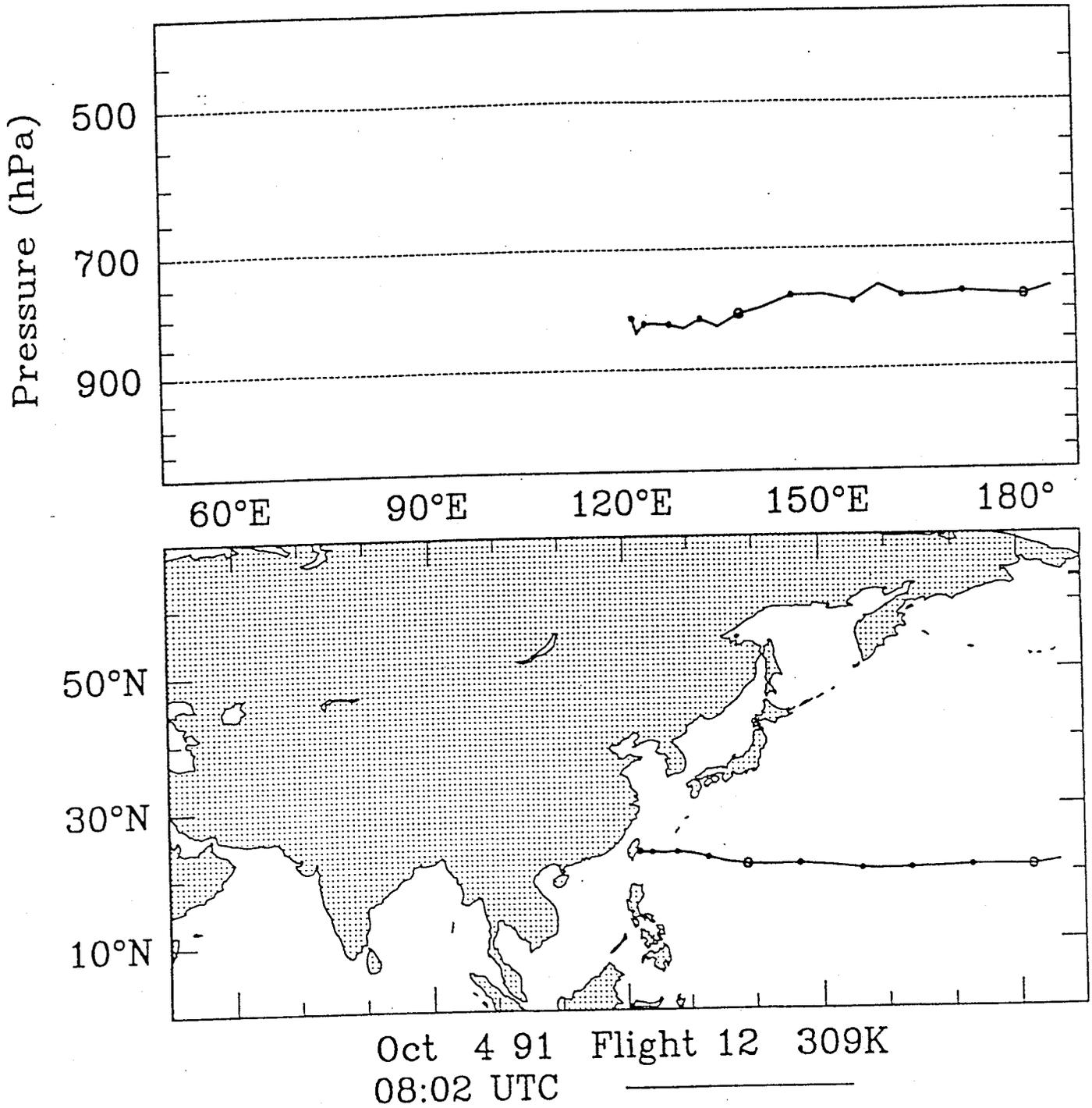


Figure 2. Isentropic air mass trajectory illustrating transport of "clean" aged Pacific air to the study region near Taiwan.

used as a basis for selecting data for Table 1 is shown in Figure 2. It is important to note that these data were synthesized from a number of flights. In most cases the vertical tropospheric column that was sampled contained a variety of layers which exhibited different chemical characteristics; That is, a variety of continental influenced air parcels were often imbedded between clean air masses. Thus, it is important to utilize both the chemistry and the trajectories to classify air masses.

Despite the fact that the mixing ratio of CO was nearly constant in the near-continental, Guam, and Southern Hemispheric "clean" air masses (Table 1), there was a distinct gradient in the mixing ratios of soluble species and activity of ^{210}Pb between these 3 oceanic study regions. We currently have no definitive explanation for this observation. The trajectories and ^{210}Pb activities suggest, however, that continental influences were discernible in air masses of "apparent" marine origin. In fact, the PEM-WEST A hydrocarbon data also support this observation (Dr. Donald Blake, personal communication, UC-Irvine). Why CO does not show this same diffuse continental impact is uncertain, but modeling results may shed some light on this phenomenon.

The data presented in Table 1 show the relative "cleanliness" of aged northern Pacific air compared to that advected from the southern Pacific. It is apparent that the Southern Hemispheric air is quite aged, and has not been influenced recently (10-20 days?) by continental sources. The aerosol species have been depleted from this air mass by wet and dry deposition processes over the southern Pacific Ocean. Note that there was no discernible vertical gradient in mixing ratios or activities in this air mass. This was the "cleanest" air sampled over the western Pacific (mission 16)

during PEM-WEST A.

Using the average data from Table 1, we have calculated equivalents-based relationships for aerosol NO_3^- , SO_4^{2-} , and NH_4^+ . These relationships are presented in Table 2. The $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio in "clean" western Pacific air has a value of about 0.1, indicating that the atmospheric aerosol is primarily a "sulfate particle." In addition, the aerosol particles appear to be quite acidic. Although not shown here, the other measured mono and divalent cation species generally contributed a small percentage to the cation composition compared to NH_4^+ . The relationships for the atmospheric aerosol in the Guam/Southern Hemispheric "clean" air are very similar to what we have observed in the remote free troposphere in other geographic locations in the Northern and Southern Hemispheres (data for other GTE missions are available from the data archive at NASA Langley Research Center).

In Table 3 we present a compilation of the data for acidic trace gases in "clean" aged Pacific air. Mixing ratios are reported for nitric (HNO_3), formic (HCOOH), and acetic (CH_3COOH) acid. It is apparent from these data that there was also a gradient in mixing ratios of acidic gases going from Southern Hemispheric air to "clean" air in the near-continental region. Again we point out the near constant values of CO over this "apparent" gradient in acidic gases and aerosol species (Table 1). As shown above for the aerosol species, the Southern Hemispheric air clearly exhibited the lowest mixing ratios encountered during PEM-WEST A. Note that the carboxylic acids were usually found in larger mixing ratios than HNO_3 . The dominance of carboxylics as acidic gases in the remote troposphere seems to be a ubiquitous finding,

Table 2. Mean Equivalents-Based Relationships for the Atmospheric Aerosol in "Clean" Air over the Western Pacific Ocean during Sept./Oct. 1991.

	Location	$\text{NO}_3^-/\text{SO}_4^{2-}$	$(\text{NO}_3^- + \text{SO}_4^{2-})/\text{NH}_4^+$
≡	Near-Continental	~0.1	2.7
	Guam/Southern Hemisphere	~0.1	1.6

Table 3. Compositional Summary for Acidic Trace Gases in "Clean" Air over the Western Pacific Ocean during Sept./Oct.1991.

Location		HNO ₃ (pptv)	HCOOH (pptv)	CH ₃ COOH (pptv)	CO (ppbv)
Near-Continental Region:	BL	60-100	150-225	100-300	70
	FT	40-60	50-250	300-450	75
Guam Region:	BL	10-40	50-200	150-250	75
	FT	20-30	50-250	50-300	75
Southern Hemisphere: (Equatorial)	BL/ FT	5-20	40-60	50-150	70

CO data courtesy of Glenn Sachse, NASA Langley Research Center, Hampton, VA.

BL means boundary layer.

FT means free troposphere.

Note: There was no discernible vertical gradient in Southern Hemispheric air.

Removed from direct anthropogenic inputs, these acidic gases appear to be the principal acidic species in the remote troposphere.

Western Pacific Air Impacted by Asian Outflow:

A significant percentage of the air masses sampled during PEM-WEST A were impacted by Asian sources. We have summarized typical mixing ratios and activities of selected aerosol species and acidic gases in Asian continental outflow. These data are presented in Table 4. A typical isentropic air mass trajectory for continental outflow is illustrated in Figure 3.

Comparison of data in Table 4 with that presented in Tables 1 and 2 gives a "first-order" signature of Asian sources for selected species. For the acidic gases, ^{210}Pb , and NO_3^- the enhancement from Asian sources over "clean" air levels is about 5-fold. Substantial enhancements were observed for NH_4^+ and SO_4^{2-} , up to 20-fold in some instances. These findings were anticipated due to the significant sulfur source from fossil fuel combustion (of low-grade high sulfur content fuels) and ammonium (i.e., NH_3) from extensive agricultural activities on the Asian continent. Note that the majority of the outflow (except for ^{210}Pb) was occurring in the boundary layer. We will describe the special characteristics of the ^{210}Pb outflow below.

Figures 4 and 5 present the vertical distributions of ^{210}Pb , SO_4^{2-} , ^7Be , and O_3 (average value over aerosol sampling interval) observed during science missions in the near-continental region (flights 6-13) and those near Guam (flights 14-19). The salient features of these distributions will be discussed below. The O_3 data was obtained by Dr. Gerry Gregory of NASA Langley Research Center (data is reported in

Table 4. Selected Aerosol and Acidic Trace Gases in Asian Continental Outflow Advected over the Western Pacific Ocean during Sept./Oct. 1991.

	HNO ₃	HCOOH	CH ₃ COOH	²¹⁰ Pb	NO ₃ ⁻	nssSO ₄ ²⁻	NH ₄ ⁺
Boundary Layer	100-500	200-1000	300-850	3-25	50-275	100-1500	300-2250
Free Troposphere	50-100	100-200	200-400	5-13	<20	20-80	20-50

Concentrations are pptv, except for ²¹⁰Pb which is stated in fCi scm⁻¹.

nss means non-sea-salt.

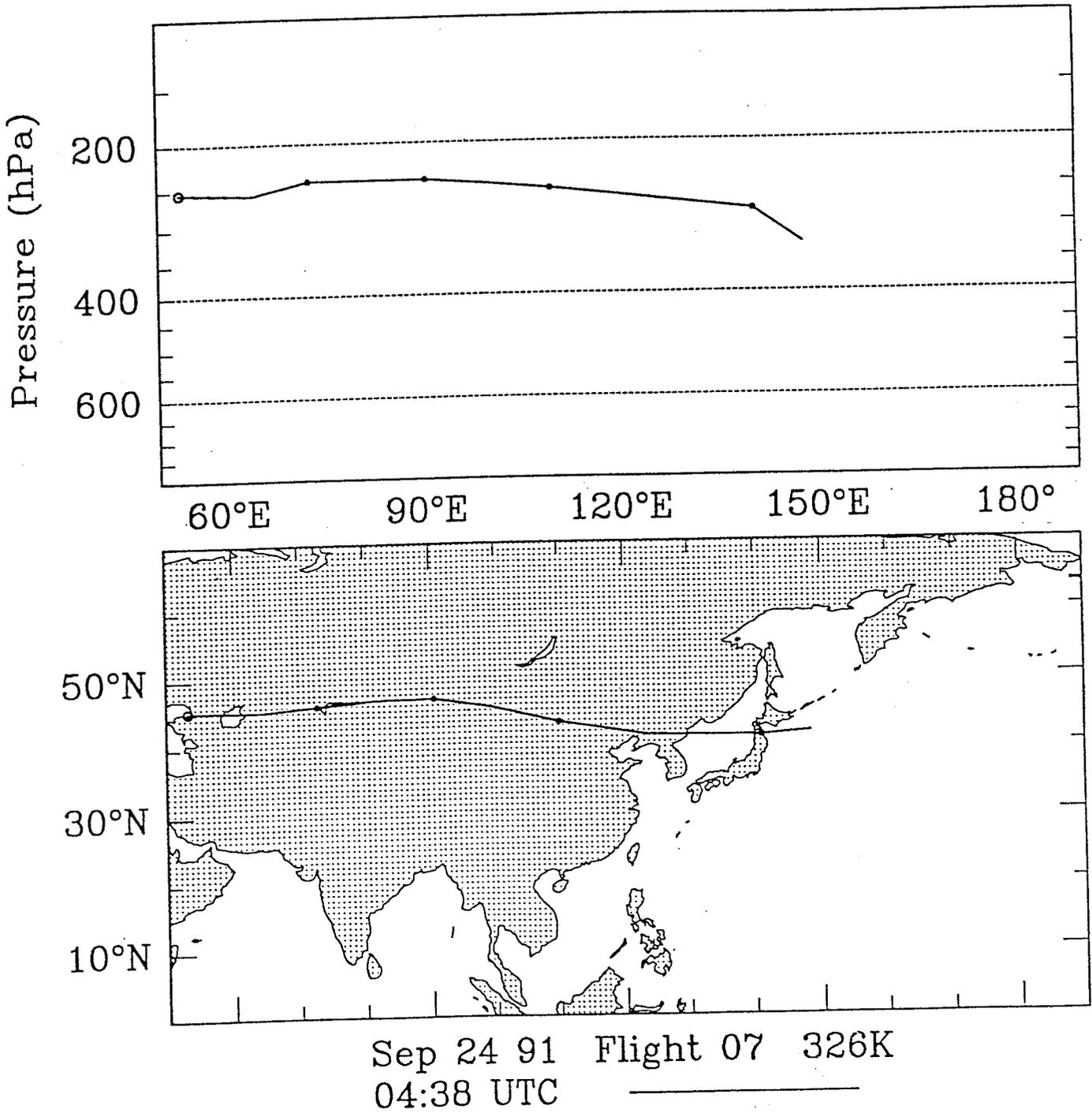


Figure 3. Isentropic air mass trajectory illustrating transport of continental influenced air to the study region near Japan.

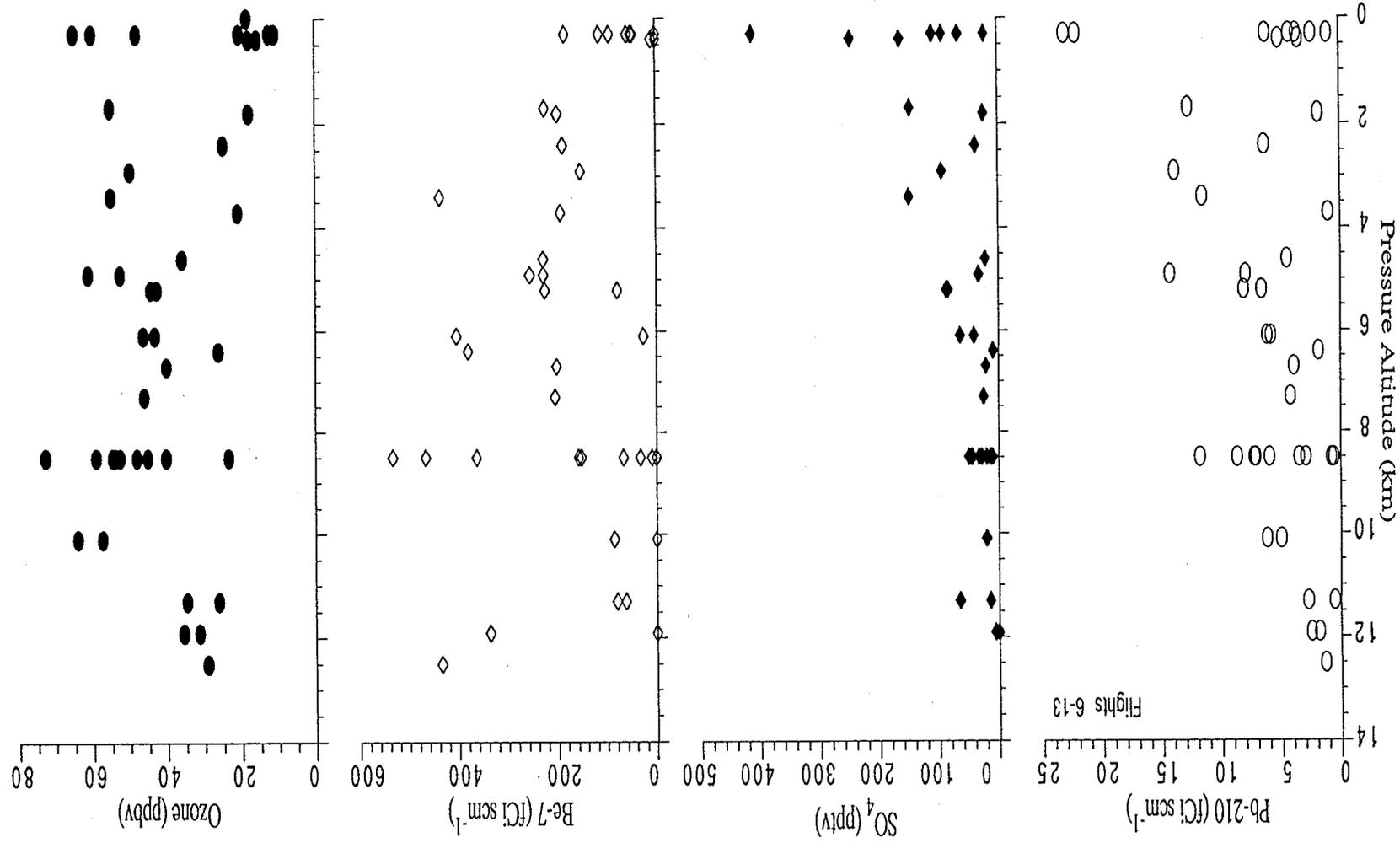


Figure 4. Vertical distribution of selected aerosol species and O₃ for flights 6-13 conducted in the near-continental region of the Pacific rim. Note that the few very high boundary layer mixing ratios of SO₄ (2000-3000 pptv) are not shown here for scaling purposes.

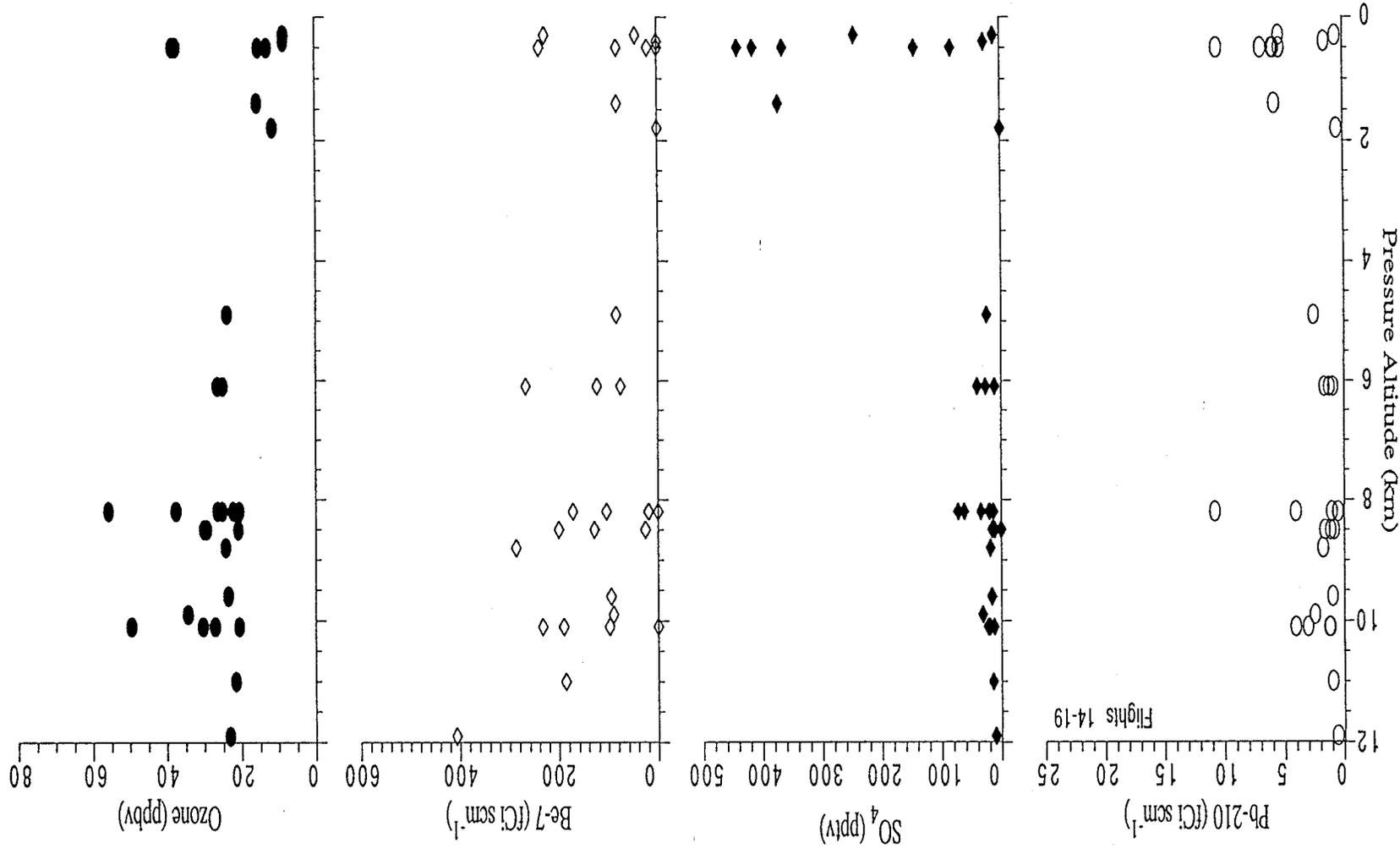


Figure 5. Vertical distribution of selected aerosol species and O₃ for flights 14-19 conducted in the region near the island of Guam.

the GTE data archive).

It is apparent from the ^{210}Pb data shown Figure 4 that continental outflow of materials was occurring at all altitudes below 10 km. Coincident with the ^{210}Pb outflow is what appears to be enhanced mixing ratios of O_3 . Particularly noteworthy is the outflow near 8.5 km altitude. Except in the boundary layer, continental outflow is barely noticeable from examination of the aerosol SO_4^{2-} vertical distribution. The same is true for aerosol species not shown in Figure 4.

A possible explanation for this observation is as follows. The precursor of ^{210}Pb , ^{222}Rn , is an inert gas that presumably would not be affected by precipitation removal processes in the troposphere. We postulate that ^{222}Rn is advected to altitudes of 10 km or so over the Asian continent by (wet) convective processes. There it decays with a radioactive half-life of 3.8 days to ^{210}Pb which quickly attaches itself to atmospheric aerosol particles. Soluble species, like SO_4^{2-} , would be removed by this convective process and subsequently not be enhanced in the upper troposphere over Asia. The dominant winds at altitude over central and northern Asia are flowing eastward at this time of year. Thus, the ^{210}Pb is advected out over the western Pacific but not soluble species which are removed by wet convective processes over the continent. Other insoluble species such as O_3 should show similar characteristics as ^{210}Pb in their vertical distributions. Indeed, O_3 's vertical distribution appears to mimic that of ^{210}Pb (Figure 4).

To explore further the possible relationship between ^{210}Pb and O_3 we show scatter plots for these species in Figure 6. For data obtained in the near-continental

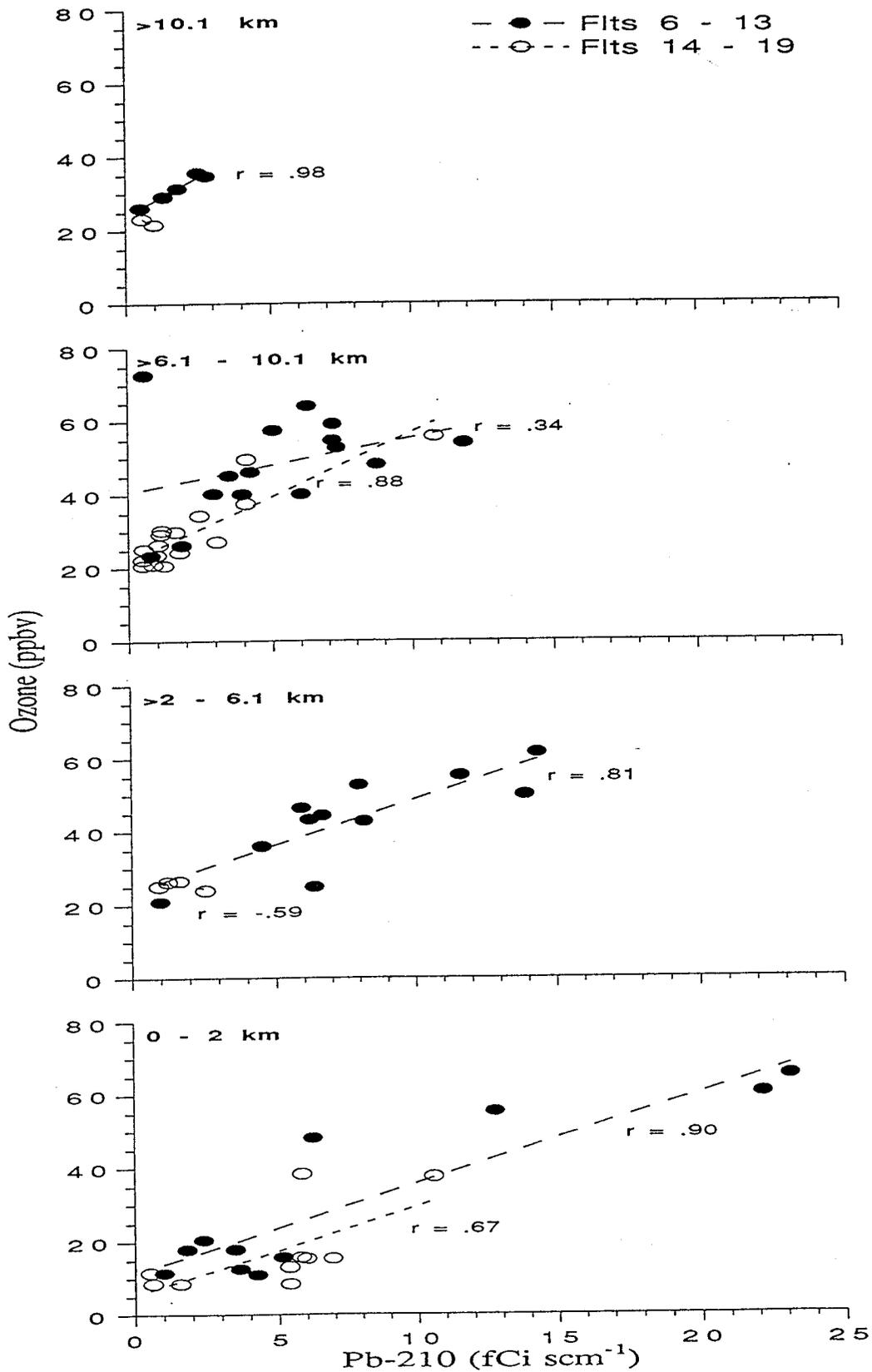


Figure 6. Relationship between ²¹⁰Pb and O₃ as a function of altitude over the western Pacific Ocean. Dashed line indicates linear regression relationship between these two species.

region (flights 6-13), ^{210}Pb and O_3 exhibit a linear correlation at all altitudes with r^2 values of 0.8-0.9. In contrast, ^{210}Pb and SO_4^{2-} are poorly correlated in these same air masses except in the boundary layer where direct outflow is not dependent on convective processes (Figure 7).

A major objective of PEM-WEST A was to examine the O_3 budget over the western Pacific Ocean. Our data may shed some light on processes affecting the distribution of O_3 over the western Pacific. Figure 8 presents a series of plots which depict the relationship between O_3 and aerosol ^7Be . In both the near-continental and Guam-based flights there is poor linear correlation between O_3 and ^7Be ($r^2 < 0.5$). The poor correlation of O_3 with ^7Be but strong one with ^{210}Pb strongly suggests that the enhanced O_3 mixing ratios in outflowing continental air masses are derived from photochemical processes rather than stratospheric inputs. Stratospherically influenced air masses in the troposphere tend to have ^7Be activities in the range of 1000 to $>5000 \text{ fCi scm}^{-1}$. Such cases were observed on the transit flights, and these will be discussed separately.

To examine continental influences in the Guam region, we refer back to Figure 5. The ^{210}Pb data suggest some influence of continental air above 8 km, but it is much more diffuse than nearer the Asian continent (Figure 4). As was the case near the continent, the aerosol SO_4^{2-} data do not readily show this Asian impact on mixing ratios. There also appears to be transport of continental influenced air in the boundary layer, and evidence for it is shown in both the ^{210}Pb and SO_4^{2-} data. We were quite surprised to consistently encounter continental influenced air masses in the

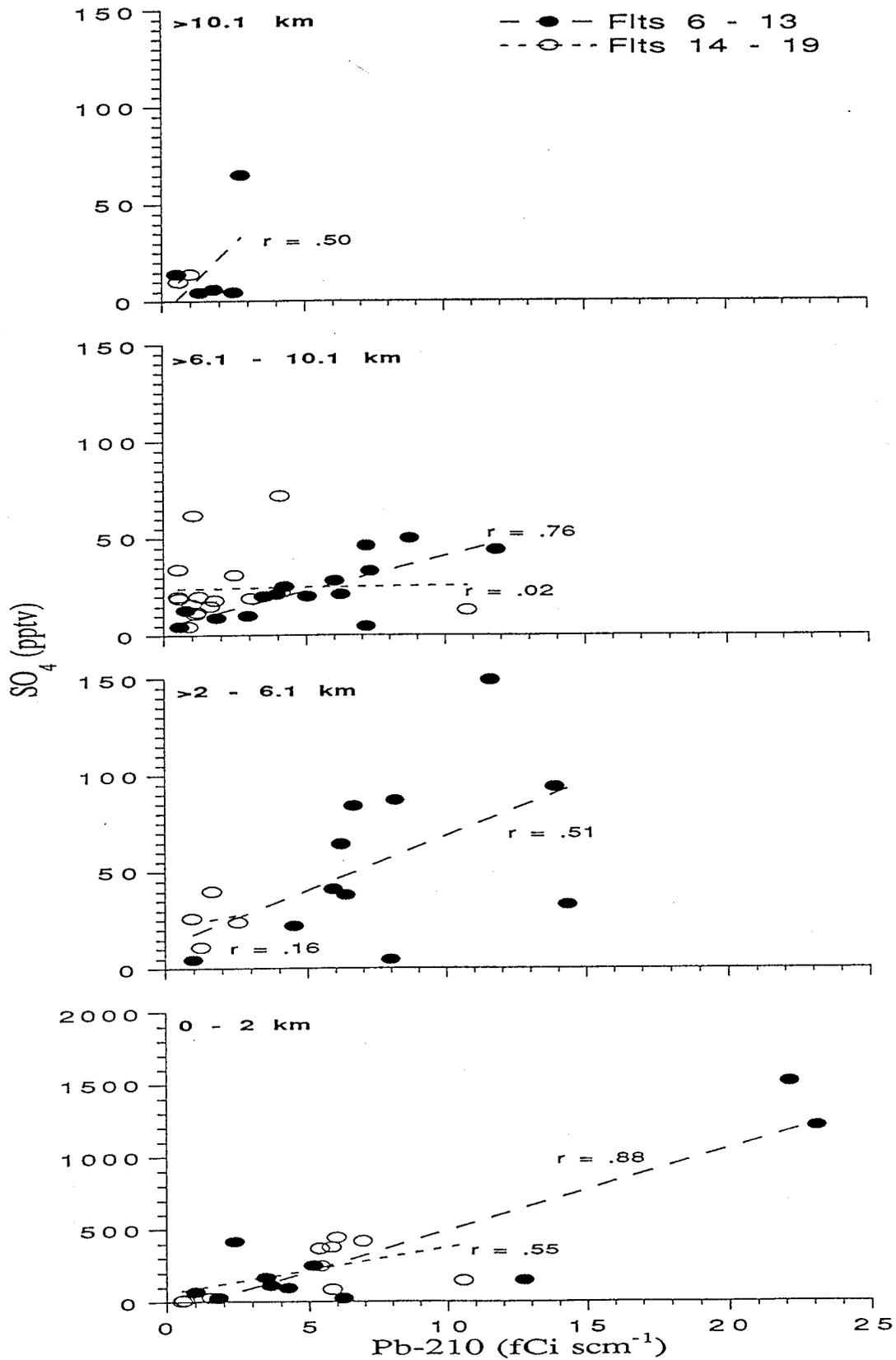


Figure 7. Relationship between ^{210}Pb and SO_4^{2-} as a function of altitude over the western Pacific Ocean. Dashed line indicates linear regression relationship between these two species.

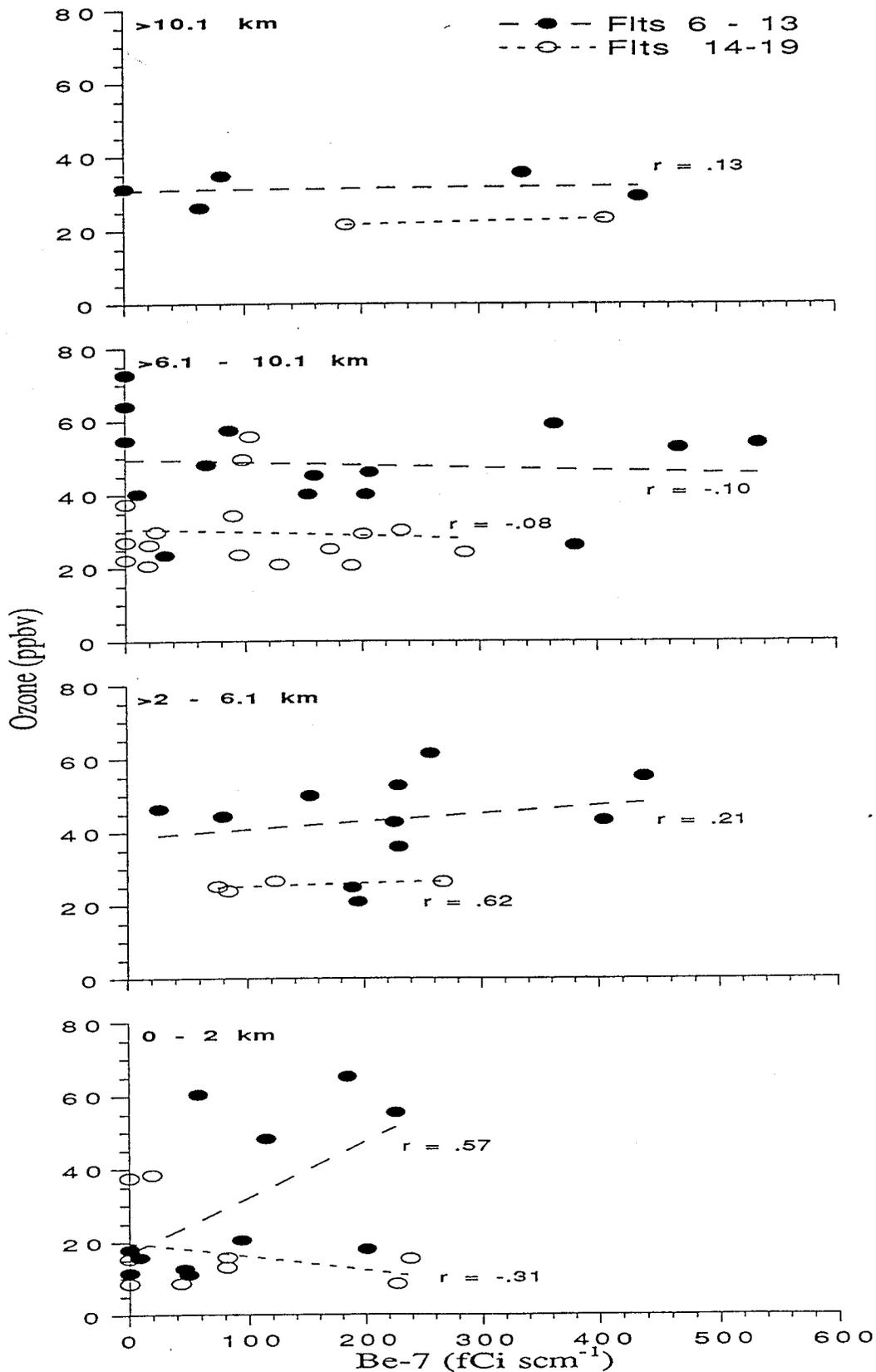


Figure 8. Relationship between ⁷Be and O₃ as a function of altitude over the western Pacific Ocean. Dashed line indicates linear regression relationship between these two species.

Guam region during this time of year. We assume that the boundary layer transport must be quite rapid, probably on the order of a 1-3 days, since these species should be efficiently removed by wet and dry deposition processes in the marine boundary layer. During the PEM-WEST A field mission we consistently observed extensive cumulus and associated precipitation in the oceanic region between Asia and Guam. We thus expect that wet deposition is probably the major sink for aerosol species over the western Pacific.

Stratospheric Influences:

During the transit flights we encountered stratospherically influenced air masses on 3 occasions (missions 4, 5, and 21). We examined some of the relationships between various species in these air masses. In Figures 9 and 10 we present the relationships between ^7Be and O_3 and SO_4^{2-} respectively. In both cases there is a strong linear correlation in the data obtained above 10 km altitude, which is directly in the region of stratospherically influenced air masses. Notice that below 10 km the correlations deteriorate significantly. Such relationships are, in fact, expected for O_3 and SO_4^{2-} with ^7Be , as all of these species have stratospheric sources. This source for aerosol SO_4^{2-} was especially enhanced during PEM-WEST A due to the eruption of Mount Pinatubo in the spring of 1991.

The question of whether the stratosphere (Mount Pinatubo aerosols in particular) was a major source of SO_4^{2-} over the western Pacific during PEM-WEST A is an important one. Detailed 3-d modeling is required to help resolve this issue. Here we make a very cursory attempt to probe this question. The slope of the

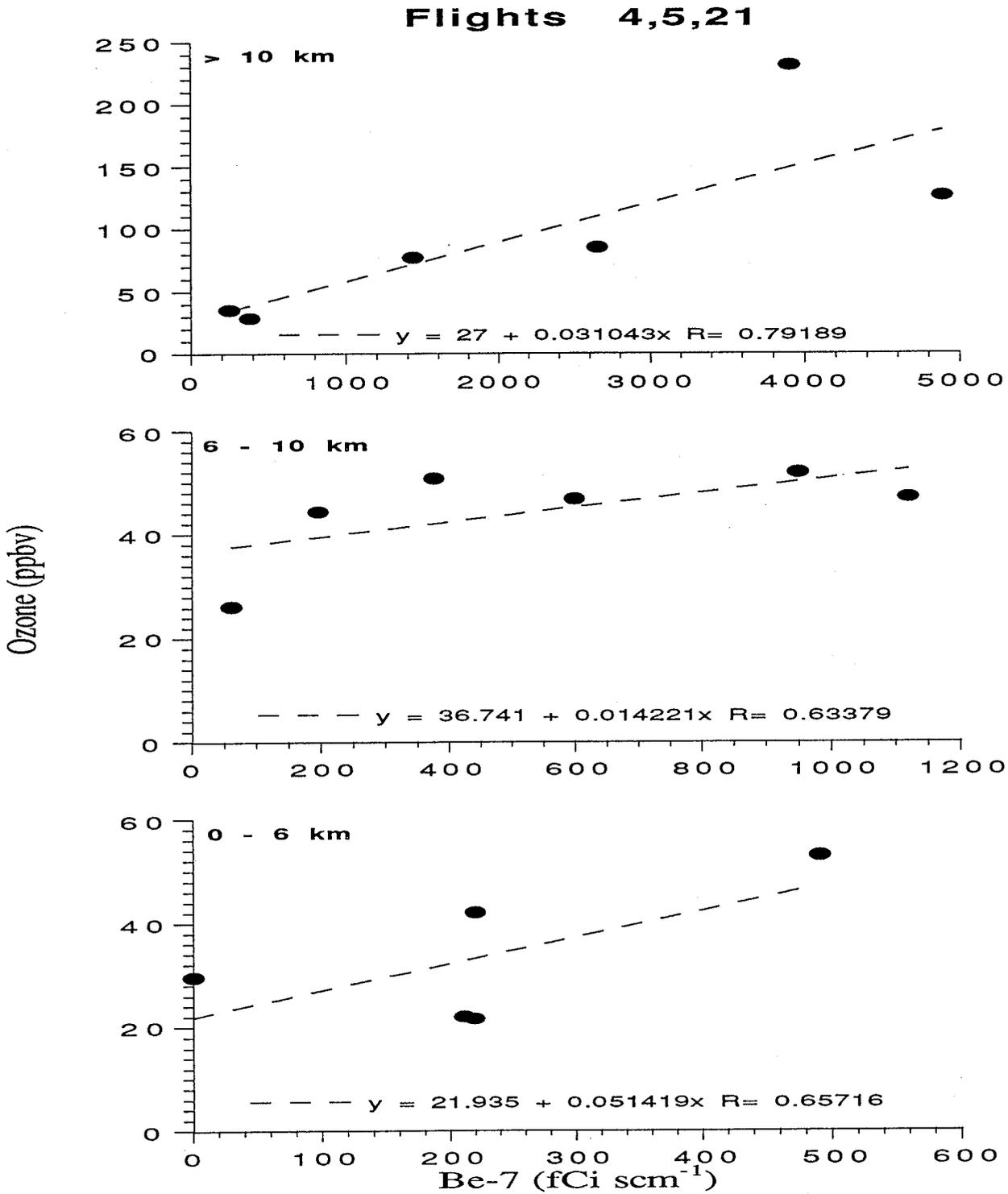


Figure 9. Relationship between ⁷Be and O₃ as a function of altitude during transit flights between Ames and the western Pacific study region. Dashed line indicates linear regression relationship between these two species.

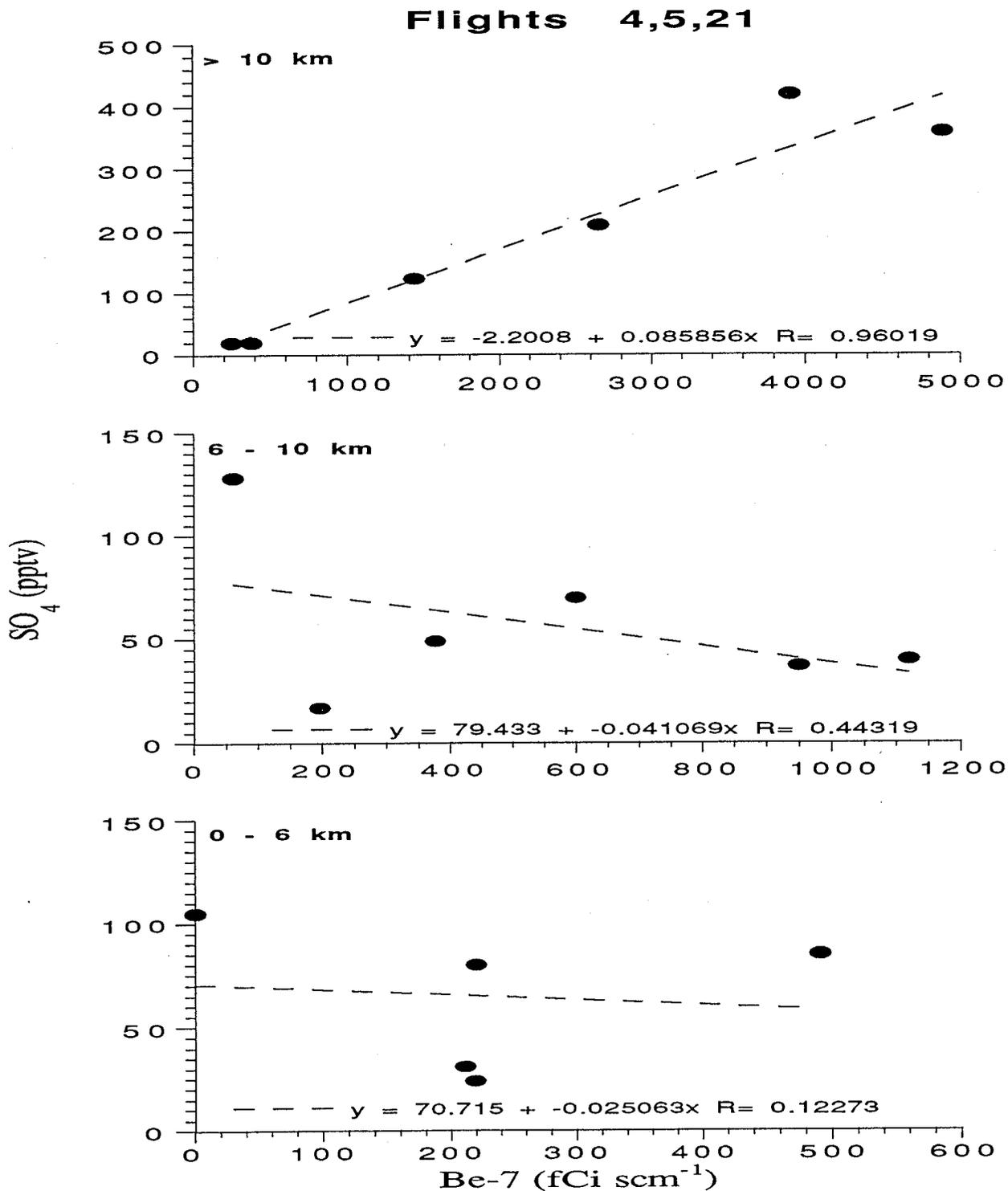


Figure 10. Relationship between 7Be and SO_4^{2-} as a function of altitude during transit flights between Ames and the western Pacific study region. Dashed line indicates linear regression relationship between these two species.

regression line for SO_4^{2-} versus ^{7}Be has a value of about 0.1, which roughly defines the fractional stratospheric input of SO_4^{2-} . Examination of these slopes at lower altitudes gives totally different results, and indicates that another source of SO_4^{2-} must be much more important below 10 km altitude. This is most likely anthropogenic sources on the Asian continent for the troposphere over the western Pacific. A similar argument to that for SO_4^{2-} can be made for O_3 below 10 km altitude (i.e., it has an important photochemical origin). However, 3-d modeling is required to begin to estimate the fractional contribution of Asian versus other sources such as the stratosphere on the tropospheric chemistry over the western Pacific Ocean. Correlation analysis only indicates the possible outcome of such modeling.

5.0 Summary of Preliminary Findings

Below we enumerate preliminary conclusions from our data collected during the PEM-WEST A field mission.

- (1) It was difficult to identify clear cases of "clean" aged Pacific air due to continental influences, however diffuse, on most flights.
- (2) The "cleanest" air masses encountered during PEM-WEST A originated in the Southern Hemisphere.
- (3) Carbon monoxide does not appear to be a good indicator of air mass "cleanliness" with regard to aerosol and acidic trace gases over the western Pacific Ocean. The reason for this is not readily apparent at this time.
- (4) In the near-continental region boundary layer air was frequently impacted strongly by Asian sources.

(5) High altitude outflow of continental air was readily apparent in the ^{210}Pb distribution but not in soluble species, presumably due to wet convective removal of soluble species.

(6) The strong linear relationship between O_3 and ^{210}Pb but the poor one with ^7Be suggests the enhanced O_3 below 10 km altitude has a photochemical origin.

(7) The stratosphere does not appear to be the dominant source of SO_4^{2-} over the western Pacific; Asian sources are potentially more important.

6.0 Publications Resulting from Work Under Grant NAG-1-1233

At this time data analysis is ongoing and several manuscripts will be written by the UNH group for inclusion in the PEM-WEST A special issue of JGR. In addition, numerous multi-authored manuscripts will utilize UNH data, and both Drs. Talbot and Dibb will be co-authors on these publications. Neither the titles or author listings are available at this time for professional publications related to the PEM-WEST A field mission.